AVERAGED LOCAL FIELD INTENSITIES IN COMPOSITE MATERIALS

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Averaged local field intensities are calculated for isotropic composites in the Maxwell–Garnett and in the effective medium theories. Exact upper and lower bounds on these intensities are also found. Implications for photophysical properties of molecules embedded in the composites are discussed.

1. Introduction

The discovery of surface-enhanced Raman scattering (SERS; see review papers in ref. [1]) and the subsequent observation of surface-enhanced absorption and luminescence [2] have pointed out the important role played by a dielectric substrate in modifying the photophysical properties of adsorbed molecules ‡. While it seems that more than one factor contributes to these enhancement phenomena, there is little doubt that a major contribution comes from the fact that the electromagnetic field is modified near the interface [4–6]. This modification is associated with excitation of surface plasmons, localized plasmons in surface protrusions, shape (lightening rod) effects and surface polarization (image) effects.

The simplest theoretical model which accounts for these effects consists of a molecule near a dielectric particle (e.g. a spheroid) [4]; the latter plays the role of an island in a surface island film, a surface protrusion or a colloid particle. The main shortcoming of this mode is the neglect of interparticle interactions. These interactions have been taken into account [5] in the Maxwell–Garnett (MG) approximation ‡ which essentially represents each particle by a point dipole. In these calculations the connection between the resonances in the absorption by island films and the enhanced Raman scattering by molecules adsorbed on such films was pointed out, however, the magnitude of the effect could not be obtained directly.

Obviously, a direct estimate of the enhancement factors for photophysical phenomena associated with molecules adsorbed on island films or embedded in composite dielectric materials should be obtained by comparing the averaged local field intensity $\langle |E|^2 \rangle$ to the incident intensity $|E_0|^2$. In this note we make this comparison for several kinds of composites. We note that theories aimed at evaluating effective properties of composite materials (e.g. the effective dielectric function

$$\epsilon_e = \int d^3r\, \epsilon(r) |E(r)|^2 / V |E_0|^2 ,$$

V being the volume of the composite and the integral

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‡ For the effect of a dielectric substrate on molecular lifetime, see ref. [3].

‡ See e.g. ref. [7]. This review article on the dielectric properties of composites includes information and detailed references on all the standard approximations. For recent developments see refs. [8,9].

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taken on this volume [7] do not normally address moments such as $\langle |E|^n \rangle = V^{-1} \int |E|^n \, d^3r$. However, such moments are irrelevant to the present problem: $\langle |E|^2 \rangle$ is associated with the absorption (and other linear photophysical properties) of radiation by optically active molecules uniformly distributed in the composite, while higher moments are relevant for non-linear optical phenomena associated with such molecules.

2. Intensity enhancement ratio for binary composites

Consider a binary composite made of two phases, 1 and 2, with dielectric functions $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ and volume fractions P_1 and $P_2 = 1 - P_1$. The magnetic permeabilities μ_1 and μ_2 are taken to be 1. Even though we take ϵ_1 and ϵ_2 to be complex functions of the frequency ω, we assume that the electromagnetic wavelengths $2\pi c/\epsilon_1^{1/2}\omega$ and $2\pi c/\epsilon_2^{1/2}\omega$ (c is speed of light) are much longer than any characteristic length of the composite so that the electrostatic limit of the Maxwell equations may be used.

We are interested in the averaged electric field intensities $\langle |E|^2 \rangle_1$ and $\langle |E|^2 \rangle_2$ defined by

$$\langle |E|^2 \rangle_i = V_i^{-1} \int_{V_i} d^3r \, |E(r)|^2, \quad i = 1,2, \tag{1}$$

where $\int_{V_i}$ denotes an integral over the volume of phase i. The enhancement ratios R_i ($i = 1,2$) are

$$R_i = \langle |E|^2 \rangle_i / |E_0|^2, \tag{2}$$

where $|E_0|$ is the amplitude of the incident field. The significance of these quantities is seen by considering a distribution of metal colloid particles (phase 1) in a host medium (phase 2) containing a low concentration of active molecules and by taking E_0 to be the field that would have existed in the pure host medium. If we assume that the molecules are distributed homogeneously within the host volume V_2, then R_2 is the ratio between the molecular absorption in the presence of the colloid particles to that in the pure host. R_1 is similarly related to the absorption by the colloid particles themselves.

The desired ratios are trivially obtained from the definition of the effective dielectric function [7]

$$\begin{aligned} \epsilon_e &= (1/V|E_0|^2) \\ &\quad \times \left[\epsilon_1 \int_{V_1} d^3r \, |E(r)|^2 + \epsilon_2 \int_{V_2} |E(r)|^2 \, d^3r \right] \\ &= |E_0|^{-2} (\epsilon_1 P_1 \langle |E|^2 \rangle_1 + \epsilon_2 P_2 \langle |E|^2 \rangle_2) \end{aligned} \tag{3}$$

in the forms

$$R_1 = \frac{1}{P_1} \frac{\mathrm{Im}\,(\epsilon_e/\epsilon_2)}{\mathrm{Im}\,(\epsilon_1/\epsilon_2)}, \tag{4a}$$

$$R_2 = \frac{1}{P_2} \frac{\mathrm{Im}\,(\epsilon_e/\epsilon_1)}{\mathrm{Im}\,(\epsilon_2/\epsilon_1)}. \tag{4b}$$

Thus we can use any existing approximation for the effective dielectric function ϵ_e to obtain R_1 and R_2 in the same level of approximation.

In the calculations presented below, we have used the effective dielectric functions ϵ_e obtained from the MG approximation and from the effective medium theory (EMT) for randomly distributed and randomly oriented spheroids ($\eta = a/b$, $a > b = c$ for prolate spheroids, $a < b = c$ for oblate spheroids, a, b and c are the spheroid axes) of phase 1 in the host medium 2 [‡]. For every given set of values of ($\epsilon_1, \epsilon_2, P_1, P_2 = 1 - P_1$) it is also possible to obtain exact upper and lower bounds on R_1 and R_2 using the bounds on the complex effective dielectric function given by Bergman [10,11] and Milton [12].

3. Numerical results and discussion

In all the cases reported below, we have used $\epsilon_2 =$ 1.0 and for the MG calculation we have assumed inclusions of phase 1 in the host 2. The behavior of the intensity ratios R_1 and R_2 as functions of P_1 is displayed in fig. 1, using $\epsilon_1 = -4.0 + 0.02\mathrm{i}$. (This is the bulk silver value for $\omega = 3.16$ eV $= 25500$ cm^{-1}) [13] In fig. 1a R_1 obtained from EMT and from the MG theory as well as the upper and lower bounds on R_1 plotted as functions of P_1. R_2 is plotted similarly in

‡ Sphere geometry is usually used in evaluating ϵ_e^{EMT}. A di calculation with a randomly oriented spheroid geometry four roots. In all cases considered here only one root had positive imaginary part and this was taken as ϵ_e^{EMT}. Obv (and in contrast to the MG theory) the geometry used in has no direct physical meaning.

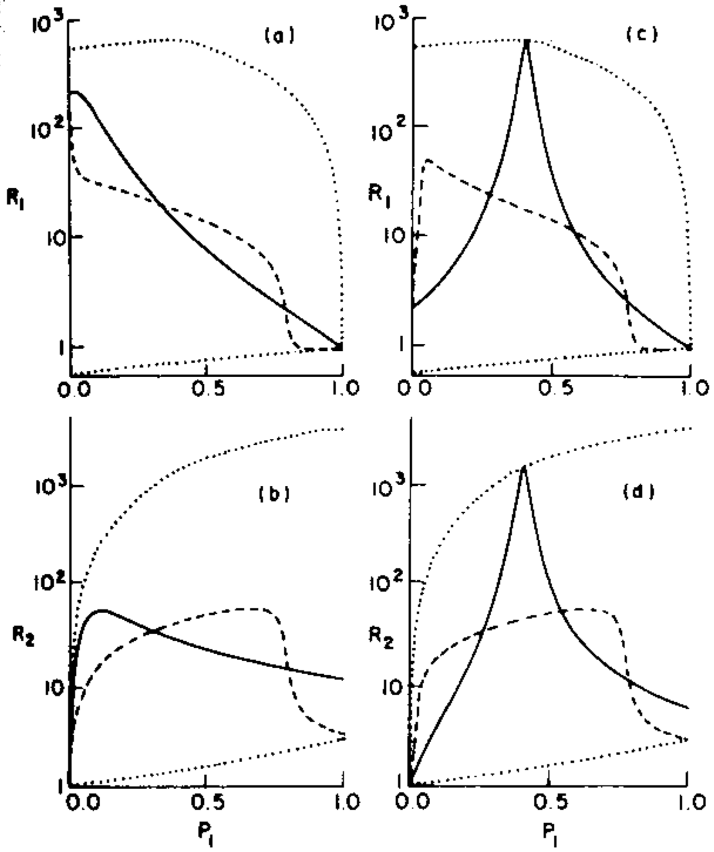

Fig. 1. Intensity enhancement ratios R_1 and R_2 as a function of composition. —— Maxwell–Garnett theory, – – – effective medium theory, . . . upper and lower bounds. $\epsilon_1 = -4.0 + 0.2i$. In (a) and (b) we use spheroids, $\eta = 1.75$. In (c) and (d) we use spheres, $\eta = 1.0$. In (a) and (c) R_1 is displayed as function of P_1. In (b) and (d) R_2 is shown against P_1.

fig. 1b. In both cases $\eta = 1.75$ (the value Re $\epsilon_1 = -4.0$ corresponds to dipolar resonance of an isolated spheroid with $\eta = 1.75$ along the long axis). Similar results for spheres, $\eta = 1$, are shown in figs. 1c and 1d. The bounds given here (and in fig. 3) were calculated using the bounds on complex ϵ_e given by Bergman [10] for a composite with a given P_1 and $P_2 = 1 - P_1$ and with isotropic (or cubic) point symmetry.

In fig. 2 the ratio R_2 is shown as a function of the spheroid aspect ratio η. EMT and MG results are shown for $P_1 = 0.01$ (fig. 2a) and for $P_1 = 0.1$ (fig. 2b).

In fig. 3 we show the results for R_2 as a function of ω where $\epsilon_1(\omega)$ is taken [13] as that for bulk silver (figs. 3a–3c) or bulk gold (fig. 3d). In these calculations P_1 was set to be 0.1. The results for silver are for $\eta = 3.0$ (fig. 3a), $\eta = 1.0$ (fig. 3b) and $\eta = 1/3$ (fig. 3c). For gold (fig. 3d) we have used $\eta = 3.0$.

The following points concerning these results should be noticed.

(a) When resonance conditions are satisfied the enhancement ratios are appreciable. Fig. 3 shows that for silver the averaged enhancement ratio for the field intensity may be as large as two orders of magnitude at $P_1 = 0.1$. Even for $P_1 = 0.01$, we may have $R_2 \approx 10$ (using MG results), namely, in a mixture containing 1% (volume) silver particles with a homogeneous distribution of molecules in the host volume we may get an order of magnitude enhancement when resonance conditions hold.

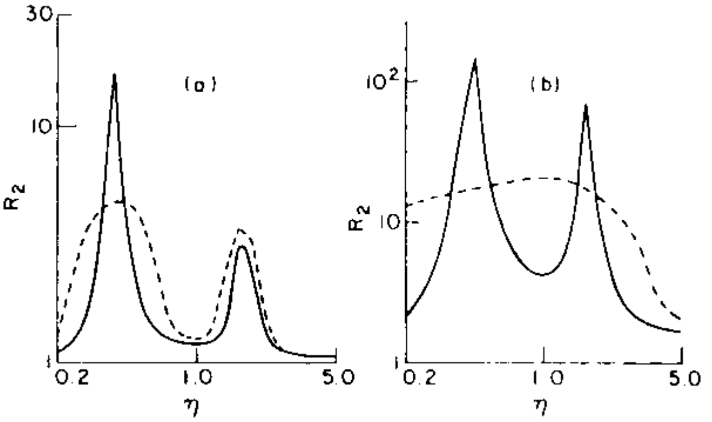

Fig. 2. R_2 as a function of the spheroid aspect ratio η. (a) $P_1 = 0.01$; (b) $P_1 = 0.1$. Line notations are as in fig. 1.

(b) The ratios R_1 and R_2 obtained as functions of the composition P_1 are significant from the practical

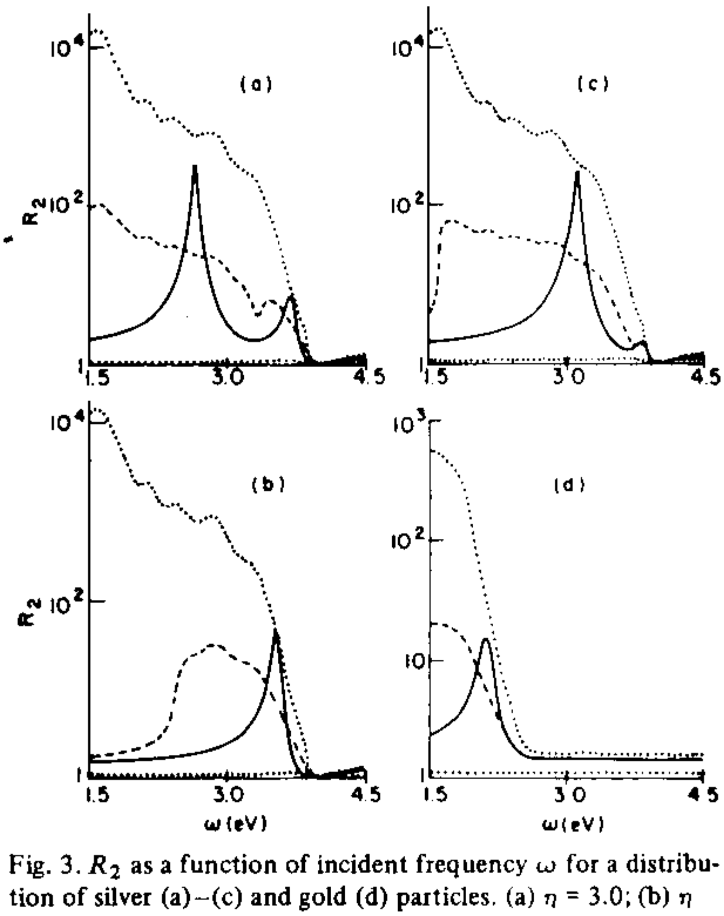

Fig. 3. R_2 as a function of incident frequency ω for a distribution of silver (a)–(c) and gold (d) particles. (a) $\eta = 3.0$; (b) $\eta = 1.0$; (c) $\eta = 1/3$; (d) $\eta = 3.0$. Line notations are as in fig. 1.

point of view. For example, it is intuitively clear that there should be some optimal composition that maximizes R_2 and an estimate of this composition is necessary for practical applications of the enhancement phenomenon. The results in fig. 1 provide such estimates within the MG and the EMT approximations.

(c) For the parameters used, no threshold behavior is observed for R_2. R_1 shows a threshold behavior at $P_1 \approx 0.8$ as seen in figs. 1a and 1c.

(d) As seen from fig. 2, disks yield on the average larger enhancement ratios than cigar shaped particles, at least for the values of ϵ_1 and ϵ_2 used.

(e) The bounds on R_1 and R_2 are, in many cases, too widely separated to provide useful estimates of these ratios. However, it is possible that some of these bounds correspond to particular choices of actual systems. If true, this means that the upper bounds displayed in figs. 1 and 3 provide realistic goals that may be achieved (for the given ϵ_1, ϵ_2 and P_1) in properly chosen systems.

(f) Although the MG and EMT approximations are usually thought to be very good at low concentrations of inclusions, this is not true close to a resonance. That is why the two approximations give such different results even when P_1 is as low as 0.01 (see fig. 2a). Any approach leading to a better approximation for ϵ_e of a composite (see, e.g., refs. [8,9]), can immediately be used to obtain better values for the enhancement ratios as well with the help of eq. (4).

4. Concluding remarks

An obvious application of the procedure described in the present note is the evaluation of ratios analogous to R_1 and R_2 for surface island films. The main differences between such systems and the system considered by us is first the essentially 2-D structure of the island film and, secondly, the (probably) preferred directionality of the islands. In the level of the MG approximation the (anisotropic) effective dielectric tensor may be obtained for the island film [13] and may be used in a way similar to the one described here to yield the enhancement ratios. Because of the anisotropy, the latter will depend on the direction of the incident field in addition to the parameters discussed here. Results for this system will be presented elsewhere.

The enhancement ratios obtained here provide only rough estimates. As noted above, both the MG and EMT approximations fail in the vicinity fo a resonance. Moreover, the use of the bulk dielectric constants for silver and gold underestimates damping effects due to surface scattering and to radiative reaction. It is possible to incorporate these effects by modifying the values of ϵ_1. A more serious obstacle is set by the need to go beyond the electrostatic limit in many practical situations. What is needed is a theory for treating the local electromagnetic fields and dielectric properties in composites similar to that which exists for the electrostatic case [8,9].

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